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OXIDATION KINETICS OF HYDROCARBON FUELS. (U)

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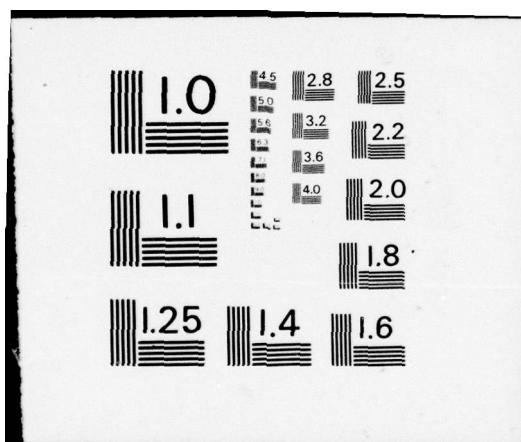
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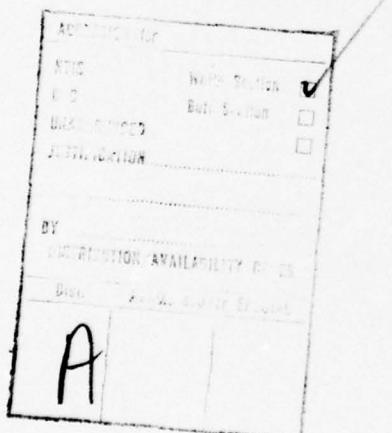
OXIDATION KINETICS OF HYDROCARBON FUELS

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SUMMARY

Interest in improved performance and reduced emission characteristics of air breathing propulsion systems and a better understanding of plume problems has created a need for better definition of the coupled fluid mechanical and chemical kinetic processes which occur in these devices. Modelling of the necessary combustion chemistry in systems using hydrocarbon fuels is difficult because of the lack of adequate kinetic data. This study is designed to determine the overall reaction rate expressions and the associated elementary kinetics for the oxidation reactions of these hydrocarbons.

A major conclusion of earlier work, besides the overall rate data reported, was that OH radical attack is not the primary mechanism contributing to the observed disappearance rates of methane (and other aliphatics through hexane) in high temperature, oxygen rich combustion. Experimental data obtained using the CO/H₂O/O₂ reaction seeded with small amounts of hydrocarbon suggest that some reaction is reforming the initial fuel at a fast rate in comparison to hydrogen abstraction by hydroxyl radicals during the oxygen rich oxidation. There does not appear to be simple overall rate expression of the form

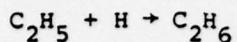
$$\frac{-d[RH]}{dt} = k_{ov} [RH]^a [O_2]^b$$

$$k_{ov} = A_{ov} e^{-E_{ov}/RT}$$

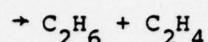
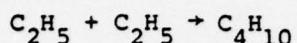
for disappearance of the primary fuel, (RH, for paraffins other than methane). Recent work has established that there are three stages in the paraffin oxidation process that must be considered if there is to be global modelling. The new element discovered is that there is a well-defined initial step very much like a pyrolysis sequence. This step is the relatively isoenergetic conversion of the paraffin to the olefin.

In addition studies of ethane pyrolysis have been completed. Results suggest that at flow reactor temperatures, the major termination step of the

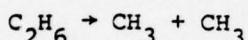
kinetic mechanism is



rather than



as suggested by other investigators. Preliminary determinations of the rate constant for



have been obtained and are in good agreement with values available from other studies.

Previous work in metal combustion led to an exploratory study of a number of chemiluminescent metal flames with the prospect of achieving population inversions between electronic states through chemical pumping. Experiments performed to find the most desirable constituents for a chemical laser device which would operate in the visible, near ultraviolet or near infrared region of the spectrum, have not been successful, but have provided much spectroscopic information about metal vapor-oxidizer systems.

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I. INTRODUCTION

The AFOSR research efforts at Princeton are concerned with the details of both rocket and air breathing combustion processes and how fundamental physical, chemical, and aerodynamic approaches provide insight to these details. Fundamental approaches are presently oriented to give specific basic knowledge about the chemical kinetic aspects of propellant and jet fuel systems and the relationship of kinetics to the overall combustion process, plume formation resulting from the combustion, propellant sensitivity, pollutant formation, etc. In particular the research is now concentrated on the chemical kinetic processes occurring in the combustion of hydrocarbon fuels. Work on metal vapor-oxidizer reactions related to laser phenomena which was another aspect of the program essentially has been completed this year.

II. PROGRAM APPROACH, STATUS AND RESULTS

A. Combustion Kinetics of Hydrocarbons

Interest in improving performance and the general emission characteristics of propulsive systems has created a need for developing a better understanding of the coupled fluid mechanical and chemical kinetic processes which occur in these devices. Modelling of the necessary combustion chemistry in systems using hydrocarbon fuels is impeded by the lack of adequate knowledge as to the detailed kinetic mechanism or the values of the absolute rate constants for many of the elementary reactions which are involved. It has been the intent of this research to develop a detailed description of these oxidation mechanisms through experimental measurements in a turbulent flow reactor developed earlier in this AFOSR program. Formulations of overall energy release and reactant consumption (product formation) expressions are developed as practical alternatives to the complete elementary kinetic mechanism. With these and other data, including detailed measurement of stable reactant, intermediate and product species taking part in the oxidation, a better understanding of the complete kinetic mechanism has evolved, and as has been shown in some cases, elementary rate constants for specific reactions can be measured.

Not only have the results of the current year followed along the lines proposed, but they have put the whole modelling question and overall hydrocarbon oxidation process in a better perspective while giving specific reaction rate data. Since the unique new interpretations could have only come about from the type of results obtained from the Princeton turbulent flow reactor, this device will again be reviewed. The next four subsections review some of the major results of the program and the current contract year in the broad context mentioned.

1) The Turbulent Flow Reactor

Basically, the Princeton flow reactor technique utilizes a heated cylindrical quartz duct 10 cm in diameter through which a hot inert carrier gas flows at velocities which yield Reynolds numbers in excess of 3500. (Figure 1). The reactor assembly is constructed so that the reactor walls rapidly equilibrate to the local gas temperature. Rapid mixing of small amounts of pre-vaporized reactants with the carrier is provided by radial injection at the throat of a high velocity mixing inlet nozzle. Proper adjust-

ment of carrier temperature flow velocity and reactant concentrations result in a steady, one dimensional, adiabatic reaction zone extending over a length of approximately 85 cm. Simultaneous thermal and chemical data at discreet longitudinal locations in the reaction zone are obtained by longitudinal extension of an instrumented probe. Temperature measurements are made with a silica coated Pt/Pt-Rh thermocouple, and gas samples are removed through a water-cooled/expansion quenched stainless steel sampling probe. Consistent with the long range objective of more complex hydrocarbon oxidation studies, a sophisticated gas chromatographic chemical analysis procedure which was developed in the program (69)*, permits measurements of all stable hydrocarbon species (including partially oxidized compounds) as well as H_2 and O_2 to 1% precision.

Several unique advantages of this approach should be emphasized. By restricting experiments to highly diluted mixtures of reactants, and extending the reactions over large distances, gradients are such that diffusion may be neglected relative to convective effects; thus the measured specie profiles are a direct result of chemical kinetics only. This is in contrast to low pressure one dimensional burner studies where diffusion effects must be determined analytically before useful chemical kinetic data are obtained. While this procedure has progressed significantly in its refinement, estimation of diffusive corrections remain very difficult.

Furthermore, in the flow reactor uniform turbulence results not only in rapid mixing of the initial reactants, but radially 1-dimensional flow characteristics. Thus real "time" is related to distance through the simple plug flow relations. However, the relation of a specific axial coordinate to real time is not well defined since the initial time coordinate occurs at some unknown location within the mixing region. One would suspect that initial mixing history might therefore alter reaction phenomenon occurring downstream. However, the existence of very fast elementary kinetics, which initiate chemical reaction before mixing is complete, permit rapid adjustment of the chemistry to local conditions as the flow approaches radial uniformity. Furthermore, the large dilution of the reactants and rapidity of the kinetics reduce the coupling of turbulence and chemistry to the point that local

* The reference procedure followed throughout this proposal is that the numbers in parenthesis refer to published work under this program and listed at the end. All other references are given in the text.

kinetics are functionally related to the local mean flow properties. This conclusion is experimentally supported by excellent agreement of the derived chemical kinetic data with that obtained from shock tubes and static reaction systems at other temperatures. Agreement also substantiates that the reactor surfaces do not significantly effect the gas phase kinetics. Comparison of flow reactor data from reactor tubes of significantly different surface to volume ratio also corroborates this conclusion. Finally and most important, the turbulent flow reactor approach permits kinetics measurements in a temperature range (800-1400K) generally inaccessible to low temperature methods (fast flow Electron Spin Resonance, Kinetic Spectroscopy techniques, static reactors etc.) and high temperature techniques (shock tubes, low pressure post flame experiments).

Many of the experimental studies will be carried out in a newly designed, arc plasma heated turbulent flow system reactor (Figures 2 and 3) which has been completed and constructed entirely at University expense in the Engineering Quadrangle on the main University campus. In contrast to the current flow reactor system described earlier and in which packed bed heat exchangers serve as the hot gas generator (see Dryer (66) for detailed hardware description), the new arc plasma concept will permit precise control of flows characteristics up to twice the presently available mass flow and total enthalpy while eliminating carrier contaminants (carbon dioxide, water vapor). A direct liquid gas conversion system is the source of nitrogen carrier gas. Possible contaminants from anode/cathode erosion in the plasma jet have been controlled through a composite material design derived during the custom construction of the jet (TAFA division of Humphrey's Corp., Bow, N.H.). Ions are eliminated in a recombination/mixing plenum far upstream of the reactor. Available instantaneous heating characteristics will accommodate rapid run preparation (the current packed heat exchanger system requires approximately 8 hours preparation time) and maximum system temperatures to greater than 1500K (the limit is imposed by reactor assembly materials). A ceramically lined, resistance heated inlet section mounted between the arc plasma generator and the reactor assembly has been designed to independently accommodate addition of up to two (thermally stable) reactant species as well as pre-vaporized water. This section is also necessary to produce uniform turbulent flow prior to the reactor assembly. Inlet temperature to the assembly will be monitored in this section with thermocouple instrumentation.

* This system on the Forrestal campus is to remain available for some concurrent use.

The reactor assembly itself is designed similar to the schematic of Figure 1. The main reactor tube is of fused silica ten centimeters in diameter and approximately 185 cm in length including a 28 cm nozzle inlet mixing section. Fused-silica walls further assure elimination of surface reaction effects. There are two additional reactor tube inserts available to reduce the test section diameter to 7.0 and 5.0 cm. Thus the reactor residence time range can be significantly shortened (factor of 4) and reactor surface-to-volume ratio increased (factor of 2). The reactor mixing inlet can accommodate independently controlled addition of up to 3 reactant species, including a pre-vaporized liquid. This feature is particularly important to some of the new work proposed in this document.

Gas samples will be withdrawn through a new water cooled, dynamically quenched stainless steel probe with quenching gradient of greater than 2×10^7 °K/sec. A Quartz coated Platinum, Platinum-Rhodium thermocouple with water cooled jacket will be used to measure the longitudinal reactor temperature distribution. Sampling instrumentation will be extended longitudinally through the reactor section along its center line.

Gas samples withdrawn at up to twenty discrete longitudinal positions in the reactor will be sorted at low pressure in an all glass/teflon sampling assembly presently in use. Stable species including CO, CO₂, aldehydes, alkanes, and other carbon containing species will be measured as before with a Hewlett Packard 7624 Research Gas Chromatograph System equipped with electronic integrator and a modified catalyst for Flame Ionization detection [Colket et. al. (71)]. This approach permits identical sensitivity per gram atom of carbon for all carbon containing species ($\pm 1\%$ Precision). Hydrogen, oxygen and nitrogen compounds are determined by thermal conductivity ($\pm 3\%$ Precision). Water concentration will be measured continuously with a Panametrics Model 2000 hygrometer ($\pm 10\%$ Precision).

Unlike the present system, the new reactor assembly will eventually be equipped with optical windows at several longitudinal positions. Thus some integrated spectroscopic measurements, in particular that of [OH] by absorption will be possible. This approach, when adapted, will be applied most frequently in flow reactor research concerned with elementary kinetic studies.

2) Combustion of Paraffin Hydrocarbons

Combustion of paraffins above methane has always been thought to be complicated by the greater instability of the higher alkyl radicals and by the great variety of secondary products which can form. The oxidation mechanism characteristically follows the Semenov type. In their book, Minkoff and Tipper (Chemistry of Combustion Reactions, Butterworths 1962) have reported some oxidation mechanisms of specific hydrocarbons.

At higher temperatures most have accepted the primary reaction in the system to be between the hydroxyl radical and the fuel.



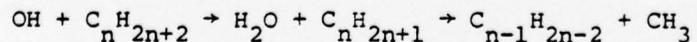
Recent work (66) has suggested that other reactions in addition to this one were important; namely, in fuel lean or rich combustion



and in fuel rich combustion



It is interesting to review a general pattern for the oxidation of hydrocarbons in flames as given by Fristrom and Westenberg (Flame Structure, McGraw-Hill, N.H. 1965). They suggest two essentially thermal zones: the primary zone in which the initial hydrocarbons are attached and reduced to CO, H_2 , H_2O , and the various radicals (H, O, OH) and the secondary zone in which the CO and H_2 are oxidized. The primary zone, of course, is where the intermediates occur. In oxygen-rich saturated hydrocarbon flames, they suggest further that, initially, hydrocarbons lower than the initial fuel form according to



Because hydrocarbon radicals higher than ethyl are thought to be unstable, the initial radical C_nH_{2n+1} usually splits off CH_3 and forms the next lower olefinic compound as shown. With hydrocarbons higher than C_3H_8 , it is thought there may

be fission into an olefinic compound and a lower radical. The radical alternately splits off CH_3 . The formaldehyde which forms in the oxidation of the fuel and fuel radicals is rapidly attacked in flames by O, H, and OH, so that formaldehyde is usually only found as a trace substance.

In fuel-rich saturated hydrocarbon flames, Fristrom and Westenberg state the situation is more complex, although the initial reaction is simply the H atom abstraction analogous to the preceding OH reaction: e.g.



Under these conditions the concentration of H and other radicals is large enough that their recombination becomes important and hydrocarbons higher than the original fuel are formed as intermediates.

The general features suggested by Fristrom and Westenberg have been confirmed in our experiments. However, this new work permits more detailed understanding of the high temperature oxidation mechanism. As stated earlier this work shows that under oxygen-rich conditions initial attack by O atoms must be considered as well as the primary OH attack. More importantly however, it has been established that the paraffin reactants produce intermediate products which are primarily olefinic and the fuel is consumed to a major extent before significant energy release occurs. The higher the initial temperature the greater the energy release as the fuel is being converted. This observation leads one to conclude that the olefin oxidation rate simply increases more appreciably when carried out at high temperatures; i.e., the olefins are being oxidized while they are being formed from the fuel.

These conclusions were based on preliminary results which were reported earlier and again given as Figures 4-7. They were further substantiated by efforts performed in this current year on the pyrolysis of some isohexanes in oxygen containing systems. These results are shown in Figures 8 and 9 and all the information is summarized in Table 1

Table 1

<u>Fuel</u>	<u>Relative Hydrocarbon Intermediate Concentrations</u>
ethane	ethene >> methane
propane	ethene > propene >> methane > ethane
butane	ethene > propene >> methane > ethane
hexane	ethene > propene > butene > methane >> pentene > ethane
2-methyl pentane	propene > ethene > butene > methane >> pentene > ethane
3-methyl pentane	ethene > propene > butene > methane >> pentene > ethane

It would appear that the results in Table 1 would contradict elements of Fristrom and Westenberg's suggestion that the initial hydrocarbon radical $C_n H_{2n+1}$ formed in the oxidation process usually splits off the methyl radical. If this type of splitting were to occur, one could expect to find larger concentrations of methane. The large concentrations of ethene and propene found in all cases would suggest that primarily the initial $C_n H_{2n+1}$ radical cleaves one bond from the carbon atom from which the hydrogen was abstracted. The bond next to this carbon atom is less likely to break since this type of cleavage would require both an electron and hydrogen transfer to form the olefin. The abstraction of hydrogen from a second carbon atom requires about 1.5 kcal less than the other carbon atoms (a tertiary carbon atom requires about 2.5 less). In a straight chain hydrocarbon there are, of course, more hydrogens on the end carbon atoms. Estimating relative probability of removal based on number and ease of removal and considering the cleavage rule mentioned indicates the proper trends designated by Table 1 and relatively large concentrations of ethene and propene. This type of estimate predicts the trends observed for 2-methyl and 3-methyl pentane and it was specifically to test the hypothesis that these two isohexanes were chosen for test. The results suggest that oxidation studies of ethene and propene should be particularly important and that insights are being obtained.

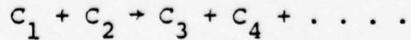
Figures 4-11 show clearly that experimentally there appears to be an initial iso-energetic, pyrolysis-like step in the overall process. Of course, this step is not exactly iso-energetic. The conversion process from paraffin to olefin is endothermic; however, some of the hydrogen formed during what is essentially a pyrolysis step does react and release energy. The two reactions are compensating energetically. Thus, the evidence is that there are three distinct, but coupled zones, in hydrocarbon combustion.

- 1) Following ignition, primary fuel disappears in a pyrolysis-like step which produces unsaturated hydrocarbons and hydrogen and would ordinarily be endothermic in nature. However, since a little of the hydrogen is concurrently being oxidized to water, the step appears to be iso-energetic.
- 2) Subsequently, the unsaturated compounds are further oxidized to carbon monoxide and hydrogen. Simultaneously the hydrogen present and formed is oxidized to water.
- 3) Lastly, the large amounts of carbon monoxide formed is oxidized to carbon dioxide and most of the heat release from the primary fuel is obtained.

Each step appears to have a different rate which depends on the temperature and presence of certain species probably radicals, and thus the importance of a given step may change.

3) Current Chemical Kinetic Modelling

The concept of overall (global) reaction kinetics and its use as we have discussed before is a direct result of the complexity of most chemical reactions and the complicated fluid mechanical situation in which some knowledge of heat release or chemical rates is necessary (ram jets, rocket engines, gas turbines, etc.). The assumption invoked is that the course of chemical kinetic events may be described in terms of a few of the main reactants and products (C_i) in a functional relation with much of the same form as an elementary reaction process. Typically, the equation is of the form:



with rate given by

$$-\dot{[C_1]} = k_{ov} \prod_{i=1}^m [C_i]^{n_i}$$

k_{ov} , the overall specific rate constant, is expressed in the Arrhenius form

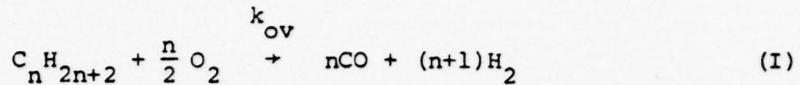
$$k_{ov} = 10^A / e^{-E/RT}$$

The n_i 's are defined as the orders of reaction with respect to C_i and $\sum n_i$ is termed the overall reaction order. 10^A and E are termed the overall frequency factor and activation energy respectively.

The relation implies nothing about the actual kinetic mechanism (in terms of elementary reactions), although the parameters in the strictly empirical relation sometimes are governed by a single elementary step (or a number of steps which basically control the rate of the chemical process. Under what circumstances such an overall correlation is usable is largely dependent on both the kinetic mechanism to which it is applied and the physical environment in which the process is occurring. Levy and Weinberg [Comb. Flame 3, 229 (1950)] concluded that the approximation is not generally applicable to chemical measurements taken in flames; however, this fact may not arise from the chemistry itself, but from the physical structure and diffusive character of the flames studied. Where a particular rate-determining step or sequence in the true chemical reaction mechanism occurs and the physical circumstances of the application are similar to those in which the expression was derived, the overall approximation is a valid and vastly simplifying idea. However, extension of such a correlation to experimental conditions outside the range studied should never be done without some reservation.

Considerable global modelling efforts have been attempted for carbon monoxide and these have been reviewed by Dryer (66) and Howard et. al. [14th Comb. Sym. p. 975 (1973)]. Methane ignition and oxidation kinetics have also been expressed in this manner, often in conjunction with developing detailed mechanisms. Many of these studies were also reviewed by Dryer (66). Avery is the only [J.A.C.S. 75, 1809 (1953)] research which has attempted global modelling of a higher paraffin oxidation (butane). Global modelling has the potential to describe only spatial energy release and reactant/final product concentrations. However, prediction of more detailed parameters such as intermediate species is not possible. Edelman and Fortune have proposed a "quasi-global" modelling

procedure for paraffin hydrocarbons as an approach to supplying these details. This technique approximates the paraffin hydrocarbon oxidation as a global reaction,



with a rate given by

$$-\dot{[C_n H_{2n+2}]} = [C_n H_{2n+2}]^a [O_2]^b k_{ov} \quad (II)$$

and combines these expression with a number of elementary reactions from the hydrogen/oxygen and carbon monoxide/oxygen reaction mechanisms. Values for a and b were assigned (a = 0.5, b = 1) and k_{ov} ,

$$k_{ov} = 1.8 \times 10^9 [(T/1111) - 0.5] T^{0.5} P^{0.2} \exp[-13,700/RT]$$

and were determined from results of an analytical study of propane ignition kinetics (Chintz and Bauer, [WSS/CI Paper 65-19 (1965)]). It was suggested that this mechanism could be applied in the temperature range 800-3000K. The assumption that a quasi-global model based on propane characteristics was applicable to higher paraffins was presumed to be substantiated by shock tube ignition delay experiments performed by Nixon et. al. These experiments identified some similarity in the functional behavior and the order of magnitude of ignition delay times for propane/and n-octane/oxygen mixtures.

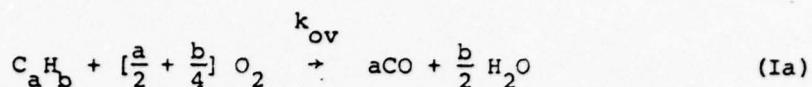
The quasi-global model thus developed has undergone some revision, as more ignition delay and elementary reaction data became available, primarily in the values of elementary rate constants for hydrogen-oxygen and CO-oxygen reactions and the expression for k_{ov} . Recent applications quote k_{ov} as

$$k_{ov} = 6 \times 10^9 P^{-0.815} T \exp[-12,200/RT] \quad , \text{ Edelman et. al. (AIAA Paper 69-86 (1969))}$$

or

$$k_{ov} = 5.52 \times 10^8 P^{-0.825} T \exp[-12,200/RT] \quad , \text{ Engleman et. al. [14th Comb. Sym. P. 755 (1973)]}$$

In accordance with earlier work [Marteney, Comb. Sci. Tech. 1, 461 (1970)], Hammond and Mellor [Comb. Sci. Tech. 4, 1019 (1971)] suggested



to replace expression (I) in preliminary analytical studies of gas turbine emissions. However, Bowman, in comments to Edelman et. al. has shown that "infinite" quasi-global kinetics do not offer any significant advantages over the partial equilibrium approach to prediction of NO_x emissions, and he concluded that these approaches were far inferior to detailed or quasi-global kinetics interpretations of methane oxidation.

It should be re-emphasized that Engleman et. al. is the only study which has attempted to experimentally corroborate the Edelman model with other than shock tube ignition delay results, and this study was restricted primarily to a comparison of experimentally measured and analytically predicted NO_x emissions. No other fundamental experimental information to which the semi-global equation might be compared has been available previously, and thus there has been no challenge or corroboration of its applicability. The studies supported in large part by this program were the first to supply some insight to this question.

4) Global Modelling of the Hydrocarbon Systems - Particularly Ethane

Clearly a new global mechanism is needed for the initial olefin formation phases of the hydrocarbon oxidation process. The oxidation of methane was studied in some detail in this program (66, 67), and encouraged the belief that the rate of reaction of hydrocarbon could be expressed by a simple global expression of the form of Equation II.

The rate of reaction in the post induction phase of the lean methane oxidation was experimentally found to be well described by the overall expression

$$-[CH_4] = 10^{13.2 \pm .2} \exp \left(\frac{-48,400 \pm 1200}{RT} \right) [CH_4]^{0.7} [O_2]^{0.8}$$

It should be noted that the parameters of this equation are significantly different than those found by investigators who have studied the induction (ignition delay) phase of this reaction in shock tubes [e.g. Skinner & Ruehrwein, J. Phys. Chem. 63, 1736 (1959); Asaba et. al., 9th Comb. Sym., p. 193 (1963); Higgin and Williams 12th Comb. Sym. p. 579 (1969)] and flow reactors [Lloyd, Proc. 6th Cong. App. Math. (1946); Mullins, Fuel 32, 211 (1953); Nemeth

and Sawyer, J. Chem. Phys. 73, 2421 (1969)]. These studies predicted the rate of reaction to be inhibited by the concentration of methane. For example Seery and Bowman, [Comb. and Flame 14, 37 (1970)] empirically correlated the ignition delay time as

$$\frac{1}{\text{Reaction Rate}} \propto \tau = 7.65 \times 10^{-18} \exp[51,400/RT] [\text{CH}_4]^{0.4} [\text{O}_2]^{-1.6}$$

However, Figure 10 shows a comparison of the overall rate constant derived by Dryer (66) with results calculated from parameters predicted by the detailed analytical studies after Bowman [Comb. Sci. Tech. 2, 161 (1970)]. An analytical overall rate constant was calculated from

$$k_{\text{ov}} = -[\dot{\text{CH}}_4]/([\text{CH}_4]^{0.7} [\text{O}_2]^{0.8})$$

Clearly there are two phases of this reaction which are not modelled by the same global parameters. Indeed, the experimental flow reactor data of Dryer (66) show similar behavior (Figure 11).

Qualitative comparison of ignition delay characteristics of propane [Hawthorne & Nixon, AIAA J. 4, 513 (1966)] and the rate of disappearance of propane in the post induction phase of its oxidation (Figure 5) are also in disagreement. It is important to remember that the semi-global modelling effort reviewed earlier was derived primarily from ignition delay data, and yet this model purports to describe finite disappearance rates of fuel during the combustion process.

Indeed, the induction (ignition) phase of the hydrocarbon oxidation with the exception of fuel rich methane combustion is generally very short relative to the post induction reaction. In fact, in some practical situations, the ignition kinetics may be totally precluded. For example, in turbine combustors, recirculation of hot, partially burned gases provides stabilization of the combustion. These hot gases contain partially oxidized reactants, combustion products, and some reactive centers, all of which may significantly reduce or even eliminate the ignition phase chemistry. The post induction phase of the reaction will remain largely unaffected, and it is this chemistry which is important to prediction of energy release rate and emissions. The turbulent flow reactor is particularly suited to study of this phase of the reaction

and can in addition provide some information about ignition chemistry in cases where it must also be considered.

Furthermore Equation II appears inadequate for describing the rate of disappearance of initial fuel in higher paraffin oxidation reactions. If one conducts an experiment at constant temperature and large concentrations of oxygen, Equation II would predict

$$-\dot{[C_nH_{2n+2}]} = \text{Constant } [C_nH_{2n+2}]^a$$

Thus a plot

$$\log \dot{[C_nH_{2n+2}]} \text{ vs. } \log [C_nH_{2n+2}]$$

should yield a straight line of slope a. Figure 12 is such a plot of flow reactor data on ethane oxidation. The non-linearity of the curve suggested that ethane disappearance rate cannot be described by a functional relation of the form of Equation II. Similar behavior had also been observed for the oxidation of propane and butane (Figures 5 and 6). Thus it appears that Equation II does not in general predict the rate of disappearance of a paraffin hydrocarbon in the post induction phase of its oxidation. Further, Figure 4 as discussed previously suggests that the paraffin reactant produces intermediate products which are primarily olefins and the paraffin is consumed to a major extent before significant energy release occurs. If the kinetics followed a mechanism represented by Equation I, there would be considerable energy release proportional to initial reactant disappearance.

In contrast, more work has substantiated that the following correlation gives a good representation of some extensive data taken with ethane:

$$-\dot{[C_2H_6]} \sim ([C_2H_6]_0 - [C_2H_6])^a$$

How well these data fit this correlation is given as Fig. 13 for the experimental data shown in Fig. 4. For nine ethane/air runs the average value of the slope, determined by the least-squares method, is $a=0.97 \pm 0.05$. There is, however, a small temperature rise in each run which contributes to the slope. Taking the temperature rise into account, the fuel dependence is reduced to the 0.80 ± 0.03 power of the amount of ethane reacted (Fig. 14) and the activation energy is about 33 kcal/mole. Experiments were made in which the initial oxygen concentrations and equivalence ratios were

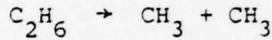
varied ($0.06 < \phi < 0.79$). A global correlation of the form

$$-\dot{[C_2H_6]} = k_E ([C_2H_6]_0 - [C_2H_6])^{0.8} [C_2H_6]^b [O_2]^c \quad (III)$$

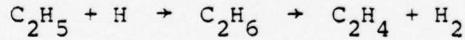
was attempted for all the data. "b" and "c" remain to be precisely defined and current estimates seem to indicate values near zero. More ethane experimentation have been performed particularly with respect to determining equivalence ratio and temperature effects more precisely. These data are now under review. This challenging pyrolysis ethane step is probably best defined by

$$-\dot{[C_2H_6]} = 10^{7.18-0.33} \exp[(-32,900 \pm 1530)/RT] [(C_2H_6)_0 - (C_2H_6)]^{0.8} \quad (IV)$$

The ethane pyrolysis studies in this laboratory [Cohen et. al. (73), Cohen (77)] have also produced elementary data for the reaction



in good agreement with other published results (see Figures 14 and 15). The reaction



has also been shown to be important to chain termination in the pyrolysis. While studies of the more complex kinetics of hydrocarbon oxidations have not as yet yielded elementary rate data, this work has produced new information of significance to developing the detailed kinetics. In particular, the research appears to point to several deficiencies in present understanding of the elementary mechanism controlling disappearance of initial fuel in the lean high temperature oxidation of paraffins.

B. Metal Combustion Laser Work

Previous work in metal combustion led to an exploratory study of a number of chemiluminescent metal vapor flames with the prospect of achieving population inversion between electronic states through chemical pumping.

Of particular interest, the low pressure diffusion flames of Mg and Ca reacting with a mixture of CCl_4 and O_2 were found to give extensive metal atom

line emission up to the ionization limit of each metal. Emissions were also observed from the metal monochloride and the high-pressure bands of C_2 . A detailed examination of these flame systems (75) has revealed that, inasmuch as high levels of non-equilibrium excitation were observed among atomic states, the flames gave neither population inversions nor excited state populations high enough to sustain the losses in a typical laser cavity.

More recently, the emissions from metal vapor/ CCl_4/O_2 flames employing the alkali metals (Li, Na and K) have been examined. These flames differed from those produced with Mg and Ca in that the metal atom excitation was much weaker and only the lowest atomic energy levels showed population. There was no metal halide emission, but the high-pressure bands of C_2 were stronger. A study of the intensity distribution of atomic states showed no population inversions. An absolute measurement of the photon yield was not made, because comparisons with the Mg and Ca photometric readings indicated that the yields from the alkali metal/ CCl_4/O_2 systems were even less than those of the alkaline earth metal/ CCl_4/O_2 systems. . .

Other systems that appeared to have some possibility by virtue of their visibly strong chemiluminescence were the alkali metal/ $POCl_3$ flames that gave polyatomic ($POCl_2$) emission in the 4100A to 5000A region of the spectrum. Inverted Polanyi flames of Li, Na and K reacting with $POCl_3$ have all been found to give the same emission spectrum except for weak atomic excitation characteristics of the metal used.

Absolute intensity measurements showed imperceptibly low photon yields based on the $POCl_3$ consumption rate. The Li/ $POCl_3$ flame gave the highest photon yield of 10^{-4} photons/molecule. Those of K and Na flames were approximately 2×10^{-5} photons/molecule and 2×10^{-6} photons/molecule respectively.

There was no visible evidence of such effects as stimulated emission and self absorption. Note, the apparatus has a multiple reflection cavity (or White cell) that can be used to detect self absorption and stimulated emission.

In summary, although these studies have produced some interesting kinetic and spectroscopic results, this work is to be discontinued on the basis that the prospects of breaking the ground for an electronic excitation chemical laser device are not promising.

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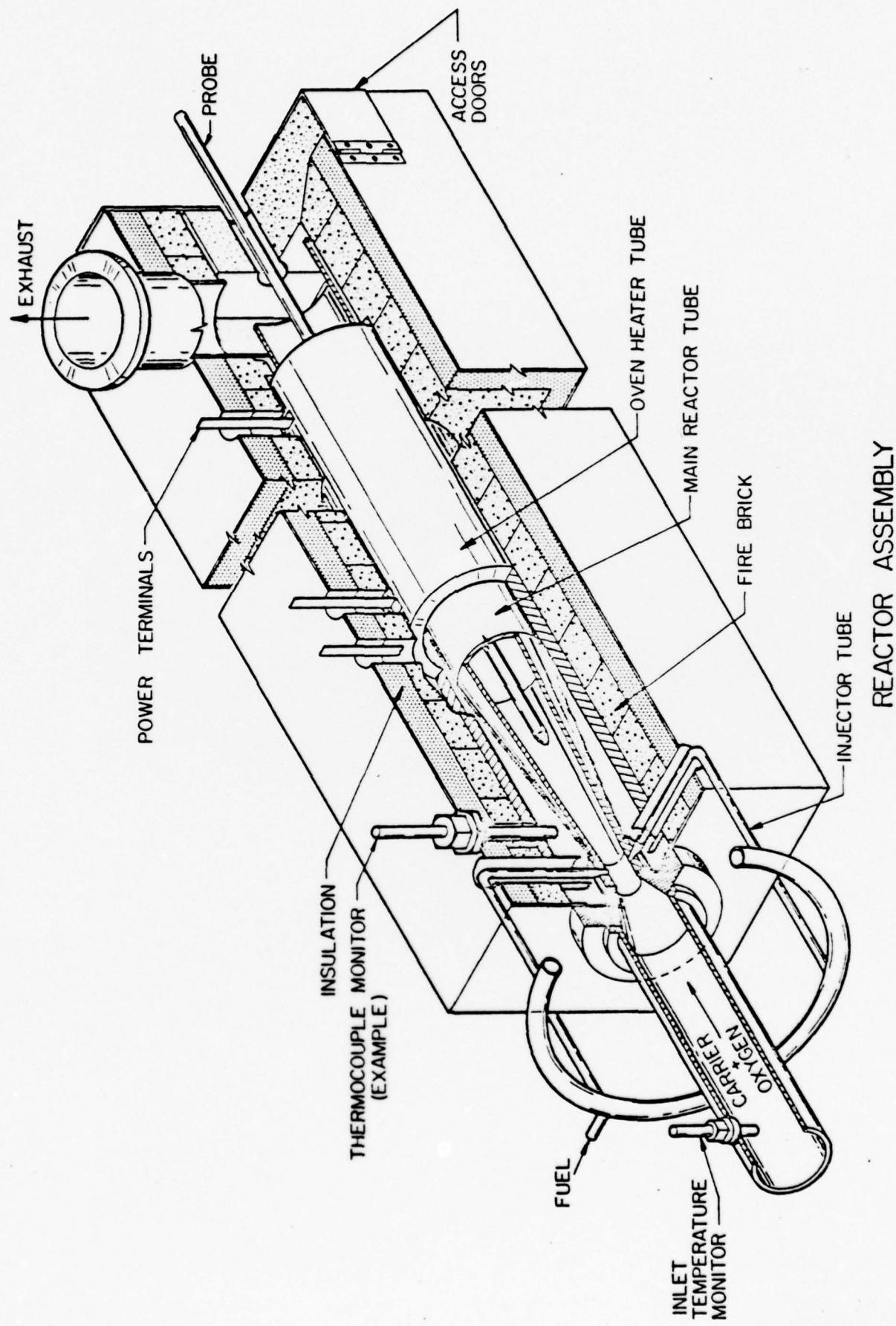
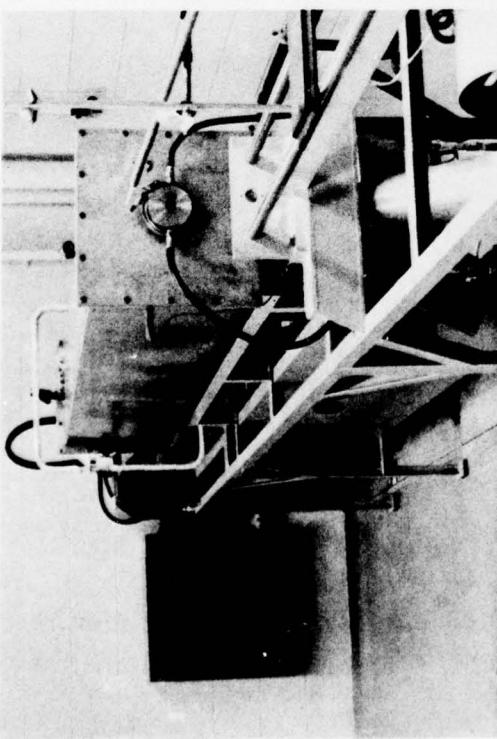
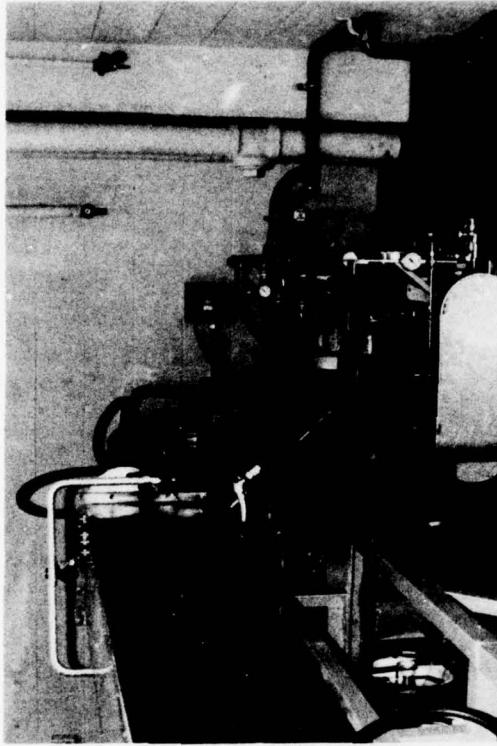


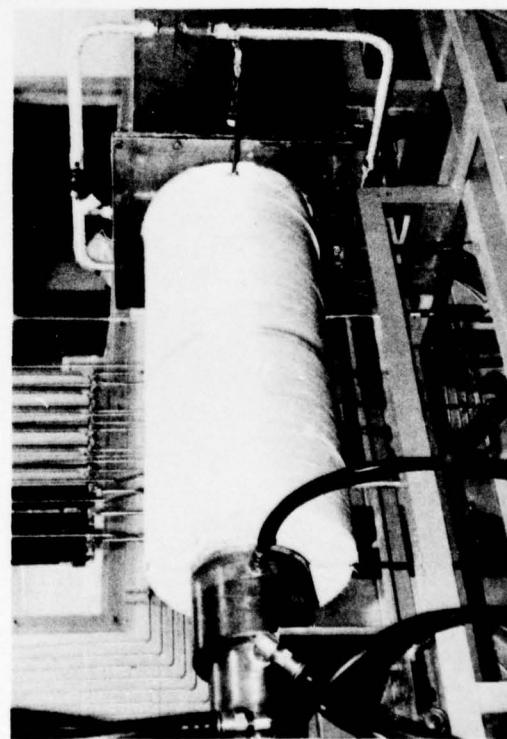
FIGURE 1



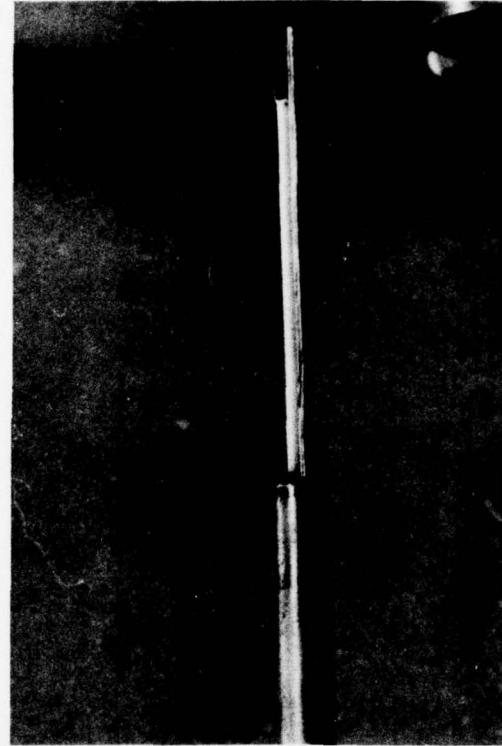
REACTOR ASSEMBLY



REACTOR ASSEMBLY AND COOLING SYSTEM

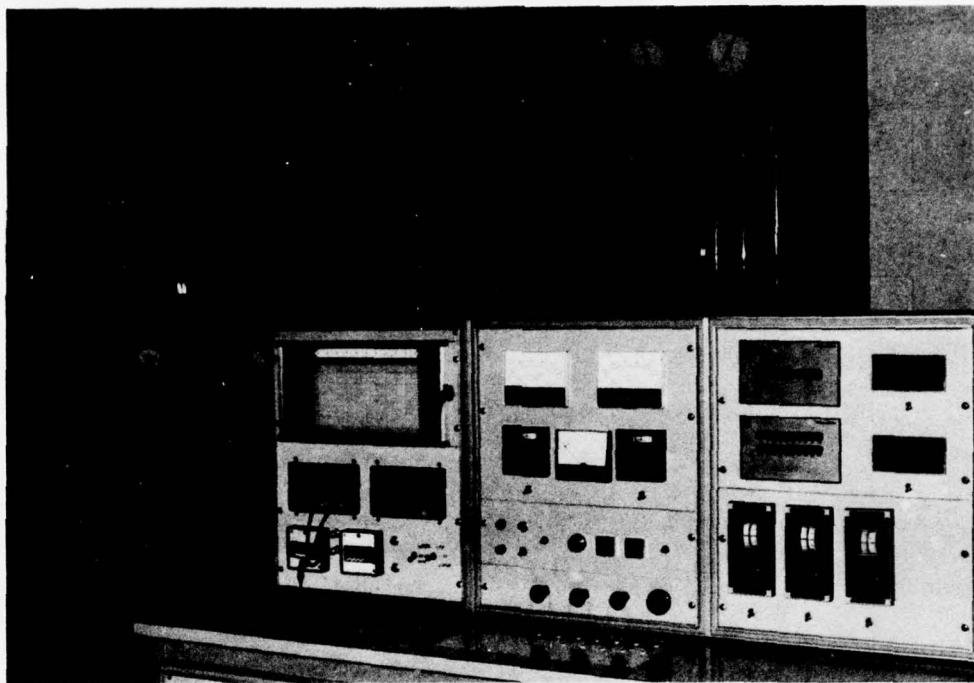


INLET SECTION AND PLASMA TORCH

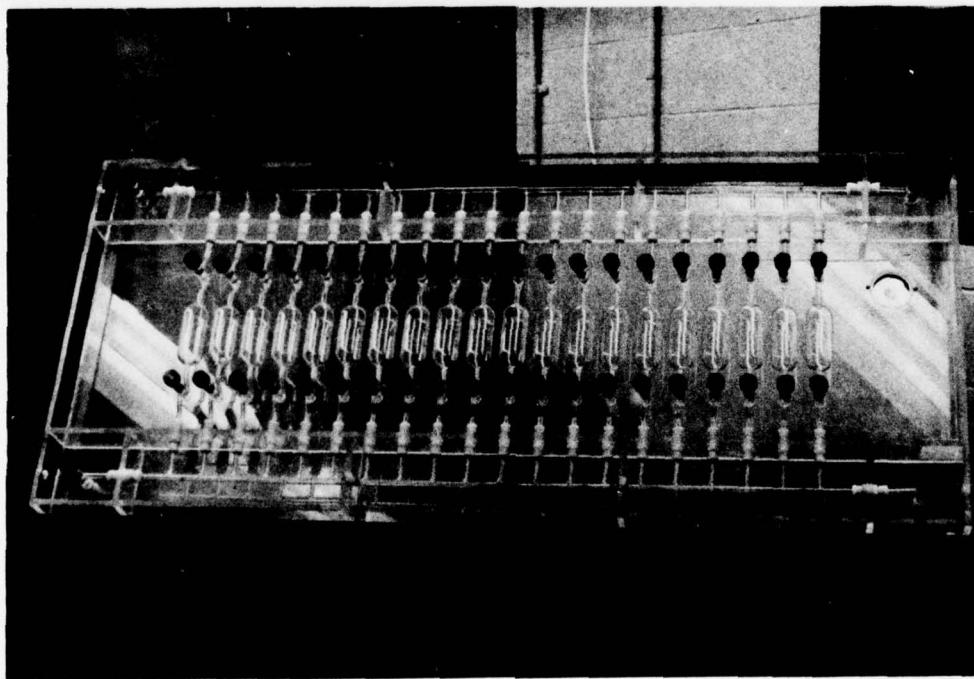


SAMPLING PROBE

FIGURE 2



FLOW REACTOR CONTROL PANEL



SAMPLING RACK

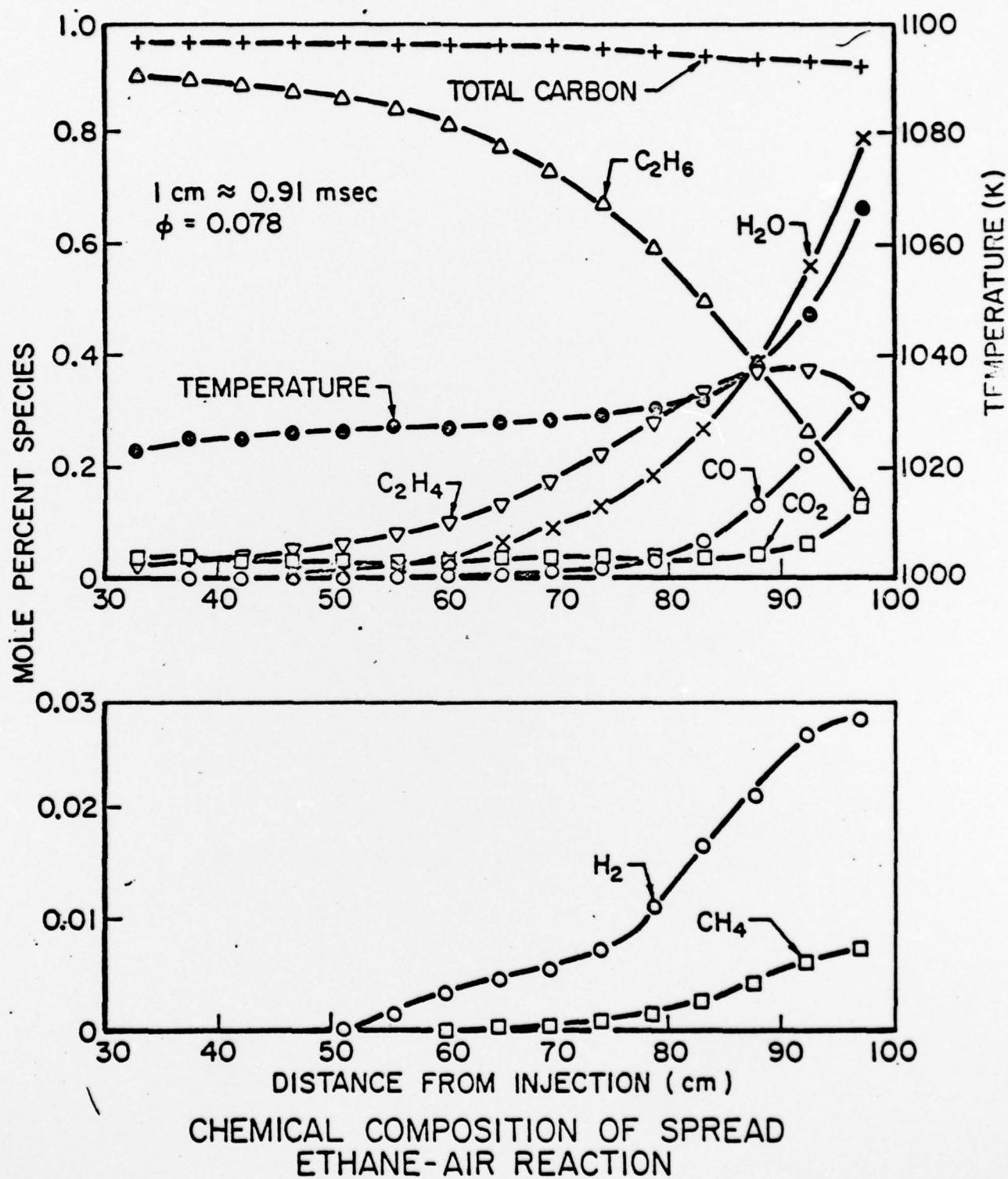


FIGURE 4

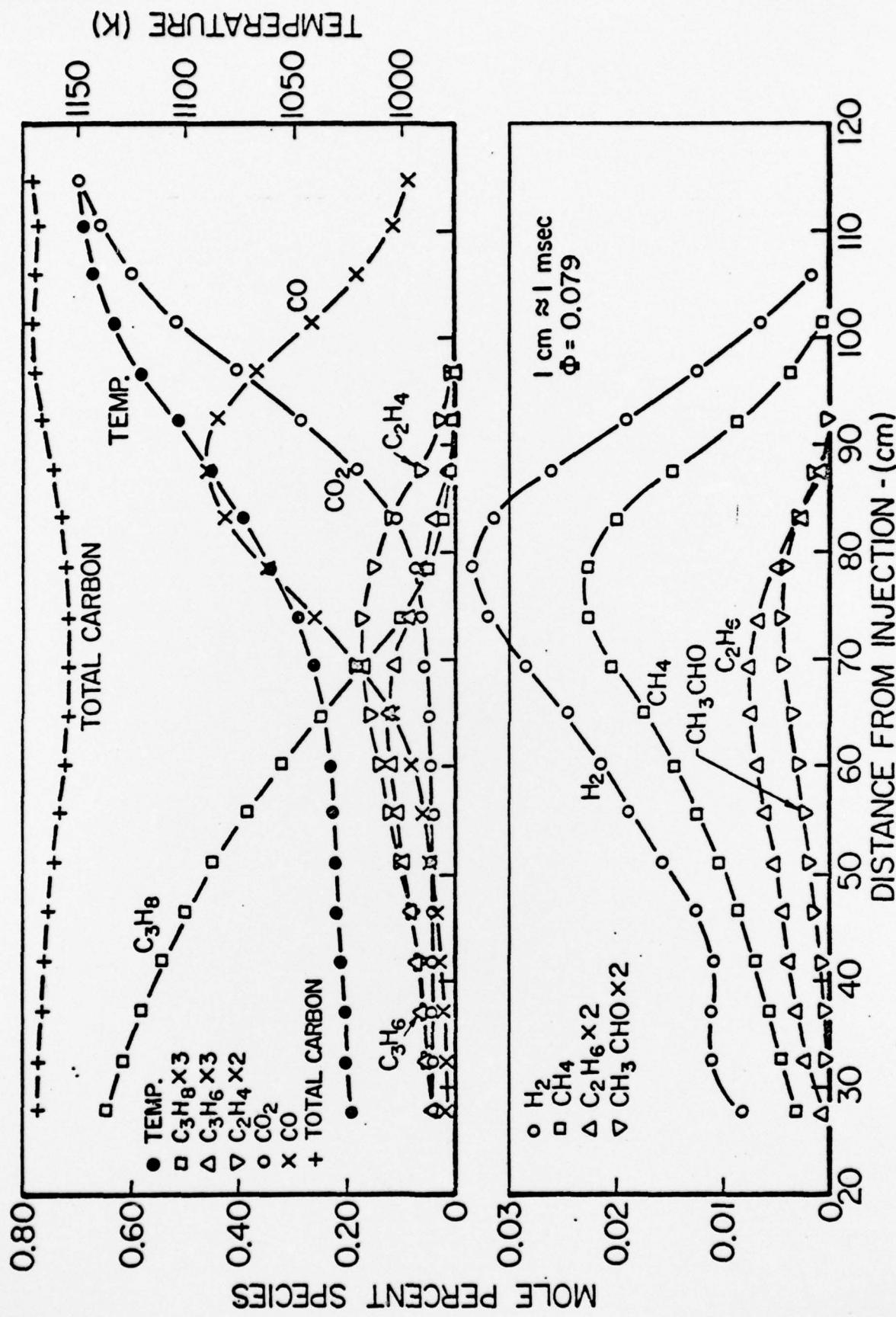
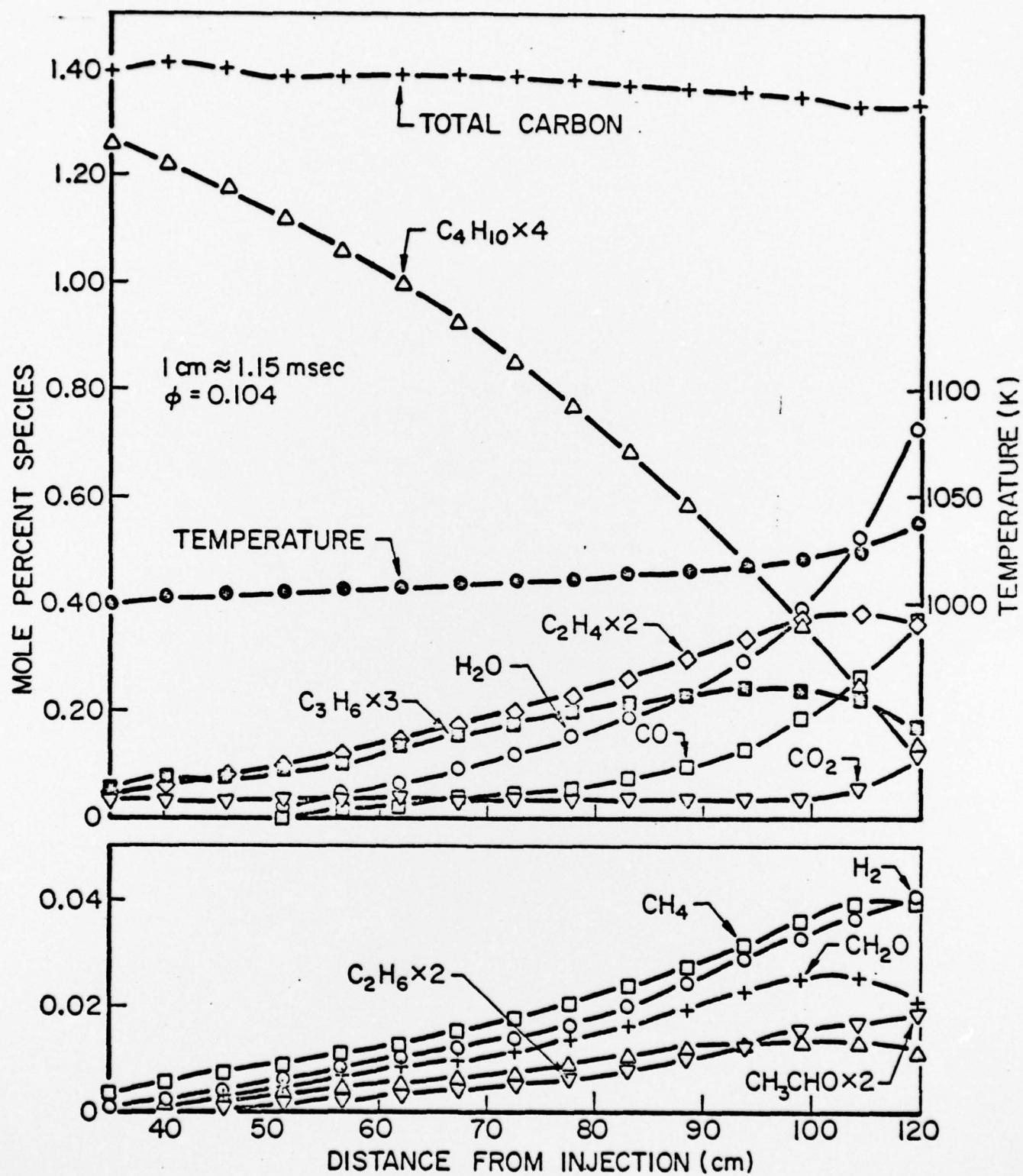
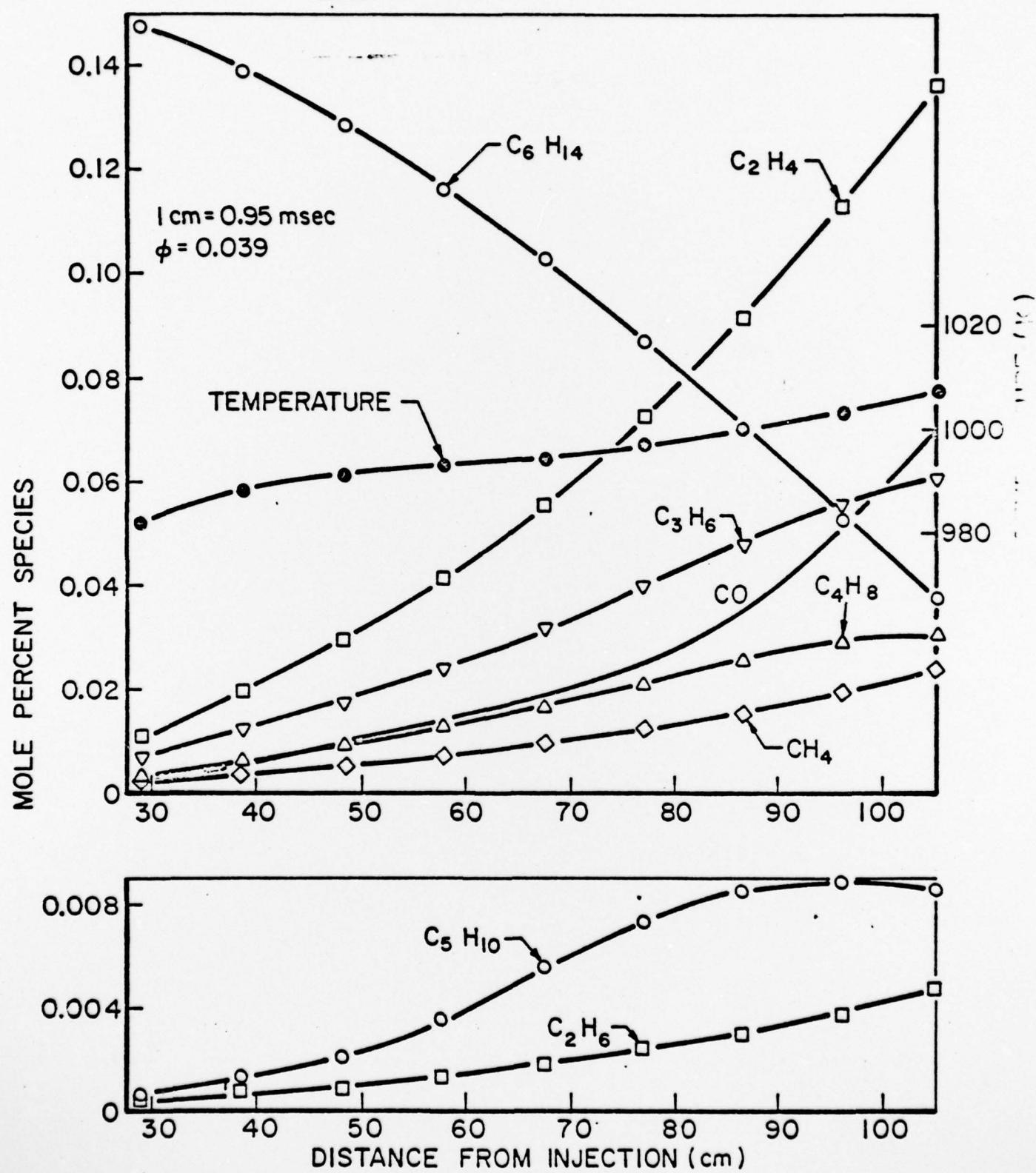


FIGURE 5



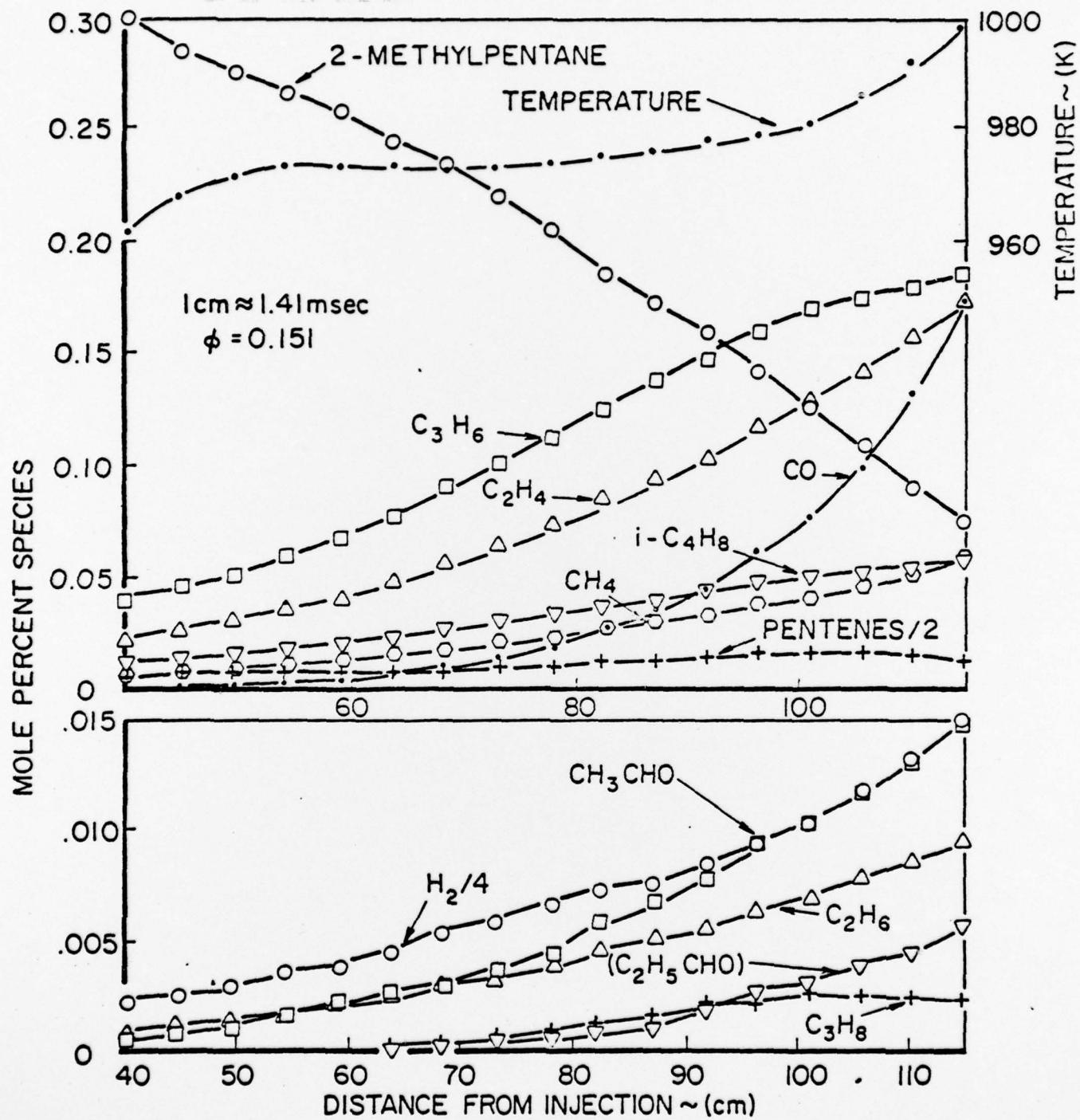
CHEMICAL COMPOSITION OF SPREAD BUTANE-AIR REACTION

FIGURE 6



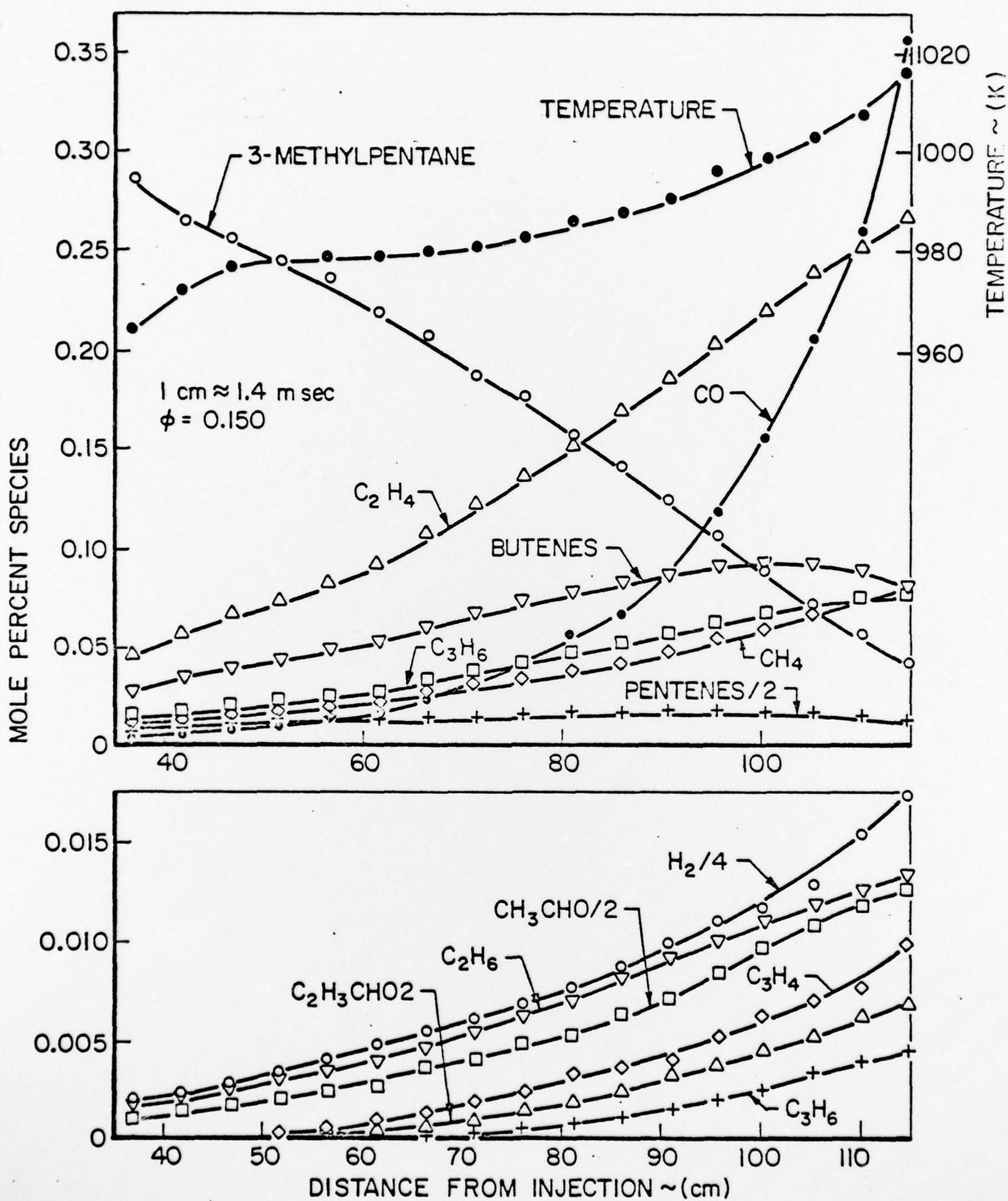
CHEMICAL COMPOSITION OF SPREAD
HEXANE/AIR REACTION

FIGURE 7



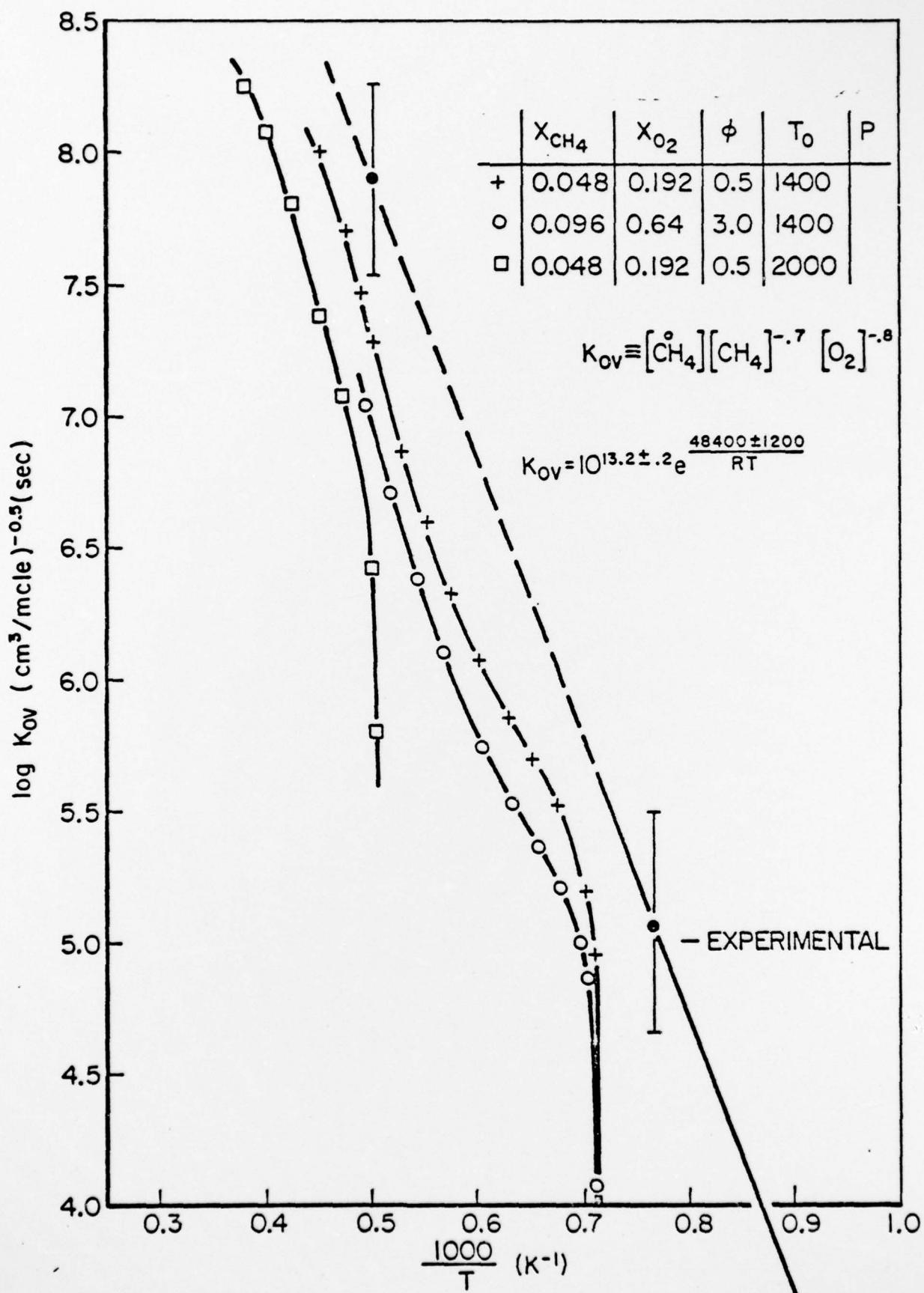
CHEMICAL COMPOSITION OF SPREAD 2-METHYLPENTANE AIR REACTION

FIGURE 8



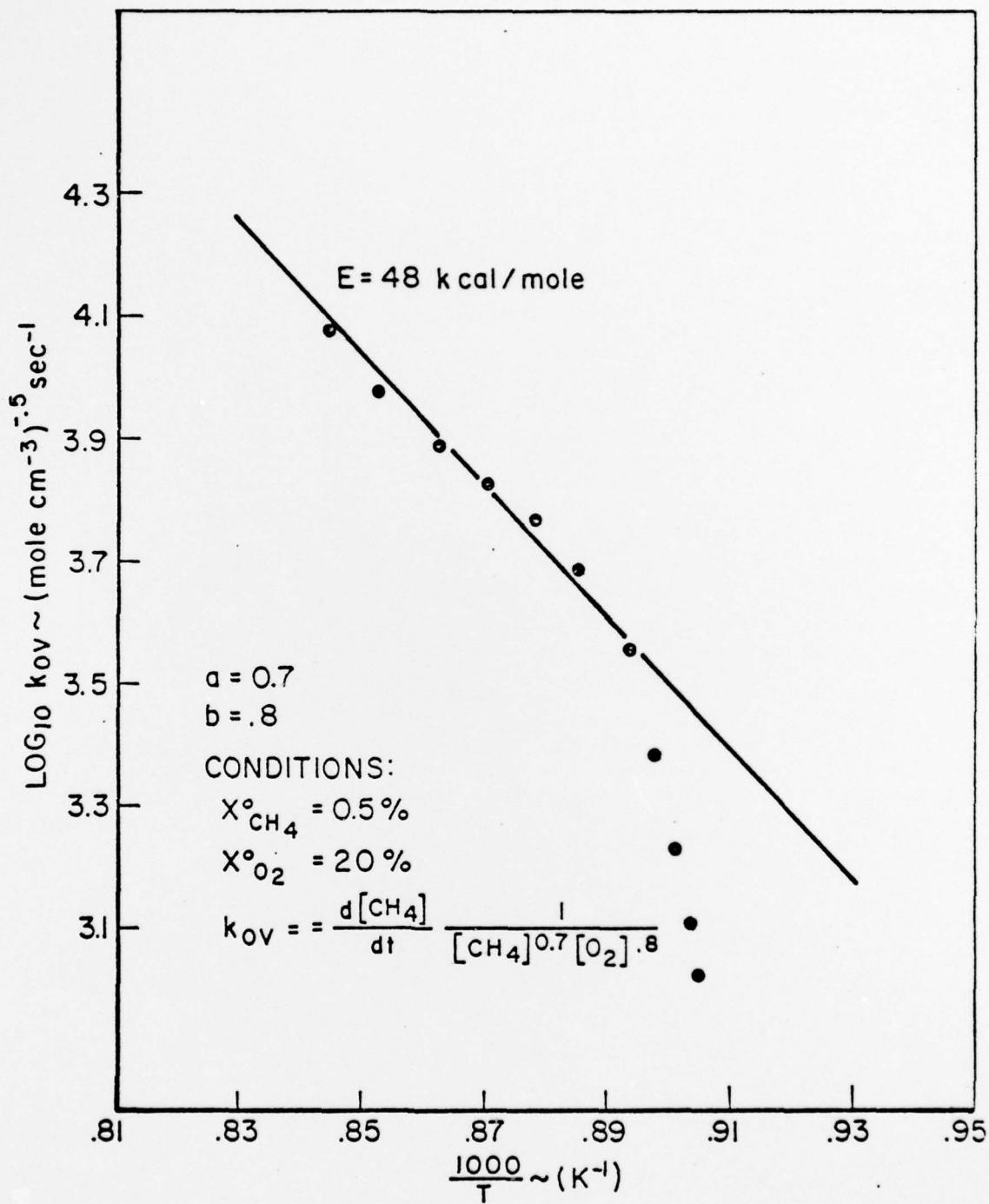
CHEMICAL COMPOSITION OF SPREAD
 3-METHYLPENTANE-AIR REACTION

FIGURE 9



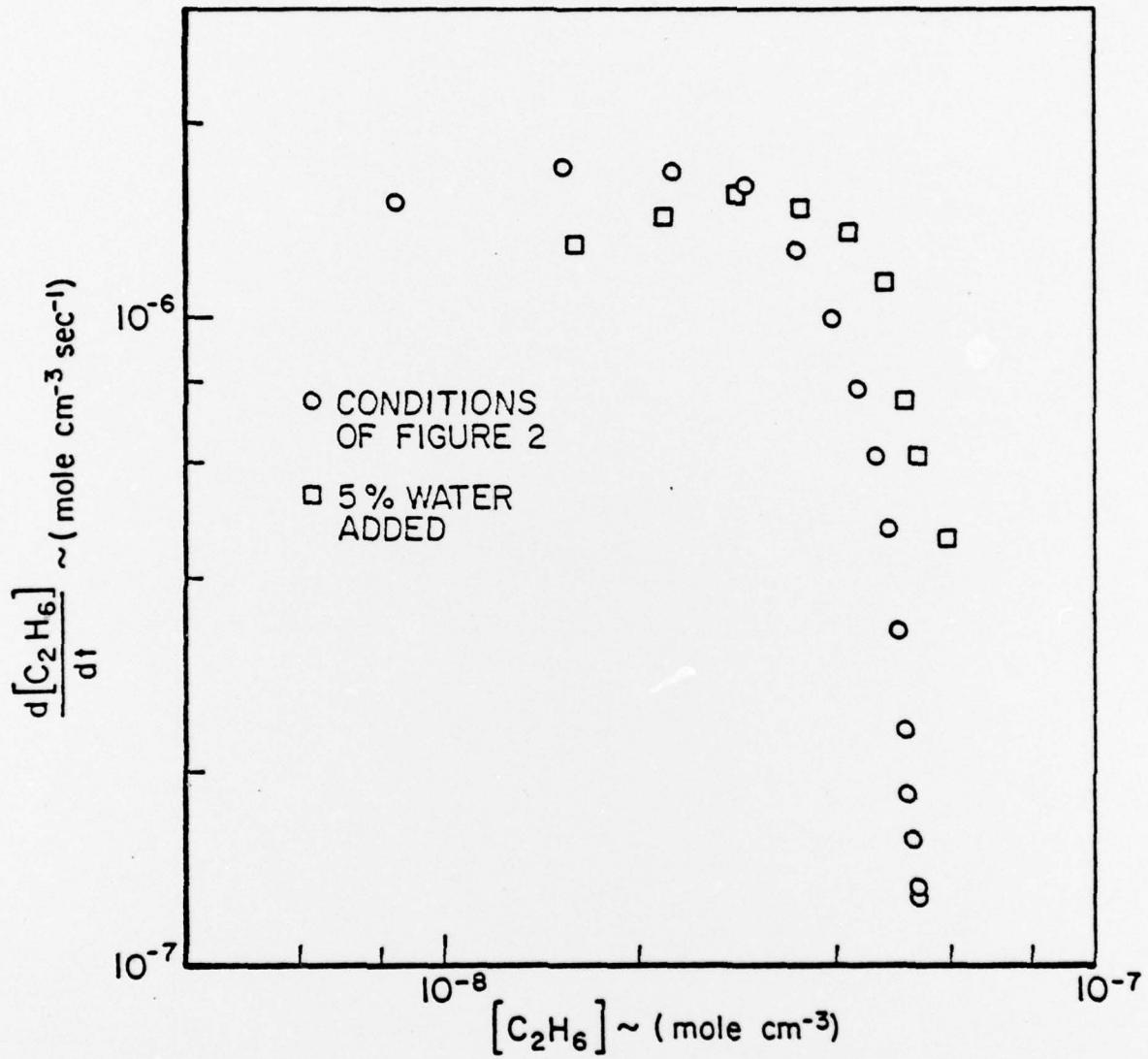
COMPARISON OF ANALYTICAL AND EXPERIMENTAL
OVERALL DISAPPEARANCE RATE OF METHANE

FIGURE 1C



DETERMINATION OF E FOR REACTION OF CH₄/O₂

FIGURE II



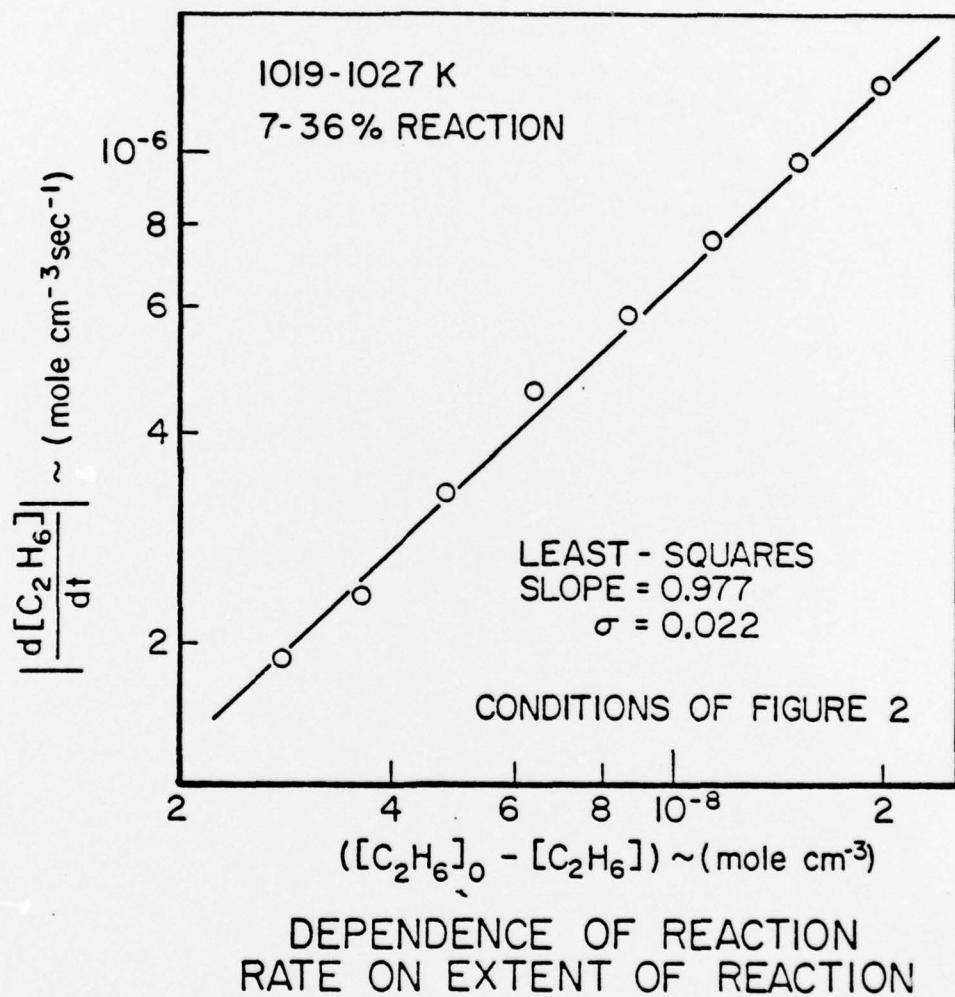
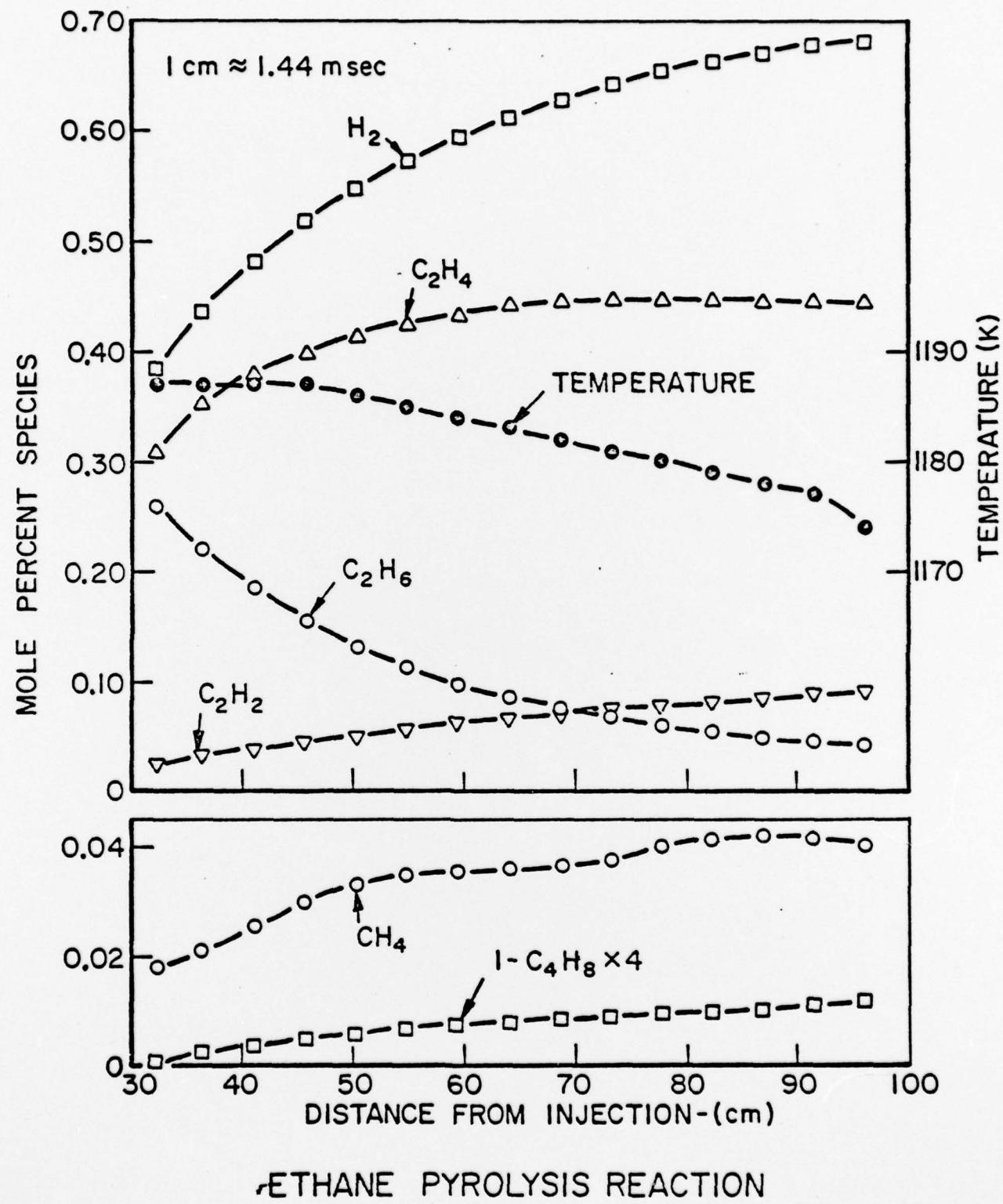
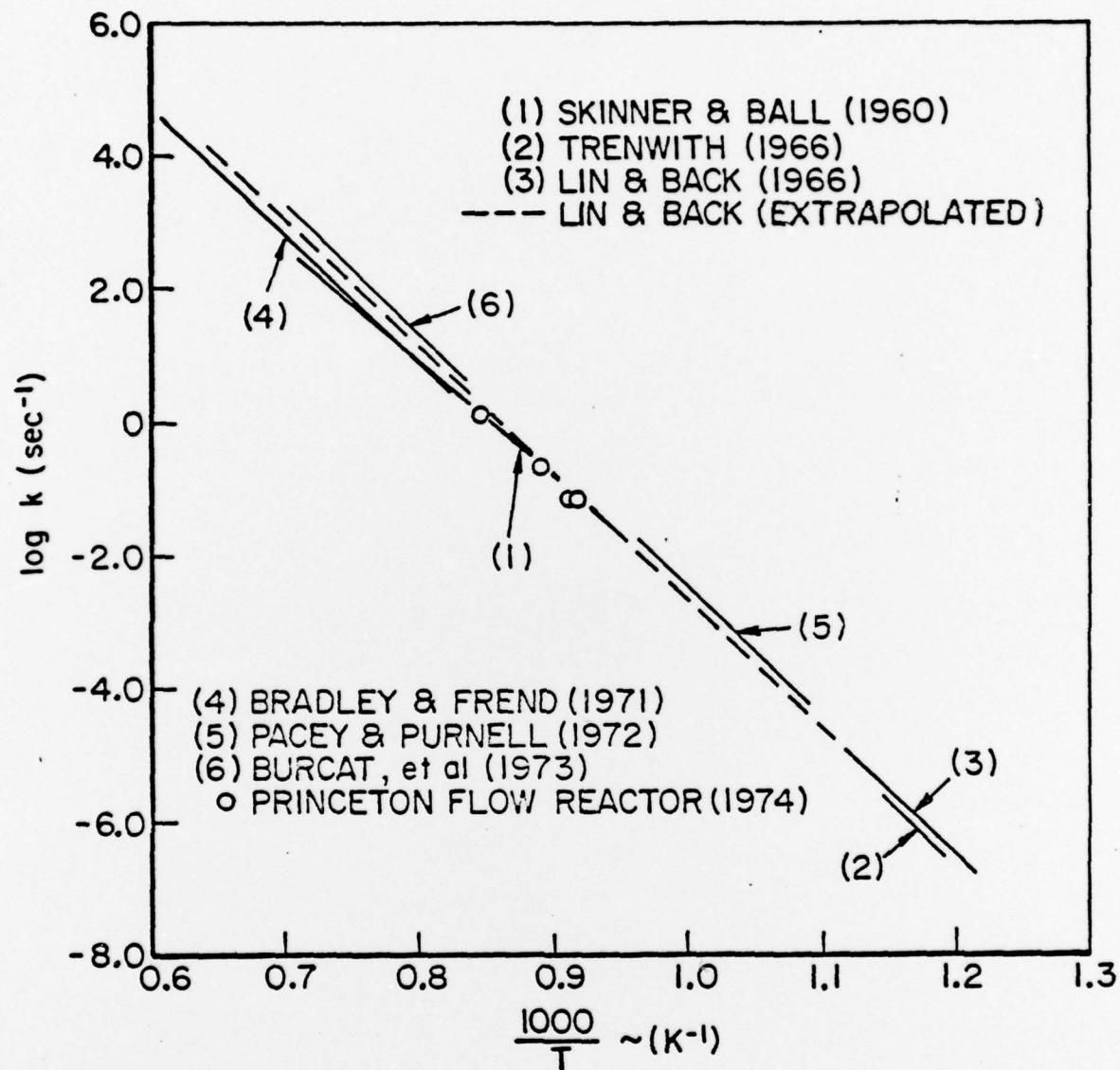


FIGURE 13



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FIGURE 14



RATE CONSTANT OF THE REACTION
 $C_2H_6 \rightarrow CH_3 + CH_3$

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17. KEY WORDS (Continue on reverse side if necessary and identify by block number)			
CHEMICAL KINETICS TURBULENT FLOW REACTOR HYDROCARBON FUELS OXIDATION KINETICS CHEMICAL LASERS FROM METALS COMBUSTION SYSTEMS			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)			
This report discusses interim results on the elucidation of high temperature oxidation kinetics of hydrocarbon fuels through experimental studies in a turbulent flow reactor. The report details current results particularly on ethane oxidation. Also discussed are results of an exploratory study of low pressure metal/oxidizer flame systems as a source of chemical laser action.			